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## **Synthesis of $\alpha$ -Amino Acids via Asymmetric Phase Transfer-Catalyzed Alkylation of Achiral Nickel(II) Complexes of Glycine-Derived Schiff Bases**

Yuri N. Belokon,<sup>\*</sup> Natalia B. Beshpalova, Tatiana D. Churkina, Ivana Císařová, Marina G. Ezernitskaya, Syuzanna R. Harutyunyan, Radim Hrdina, Henri B. Kagan, Pavel Kočovský,<sup>\*</sup> Konstantin A. Kochetkov, Oleg V. Larionov, Konstantin A. Lyssenko, Michael North, Miroslav Polášek, Alexander S. Peregudov, Vladimir V. Prisyazhnyuk, and Štěpán Vyskočil<sup>\*</sup>

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Experimental procedures.

### **Experimental Section**

**General Methods.** Melting points were determined on a Kofler block and are uncorrected. The optical rotations were measured on a Perkin-Elmer 241 polarimeter; the  $[\alpha]_D$  values are given in  $10^{-1} \text{ deg cm}^2 \text{ g}^{-1}$ . The  $^1\text{H}$  NMR spectra were recorded on Bruker AMX 200 and 400 spectrometers for  $\text{CDCl}_3$  or  $\text{CD}_2\text{Cl}_2$  solutions. FTIR spectra in solution were measured on a “Magna-IR 750” spectrometer (Nicolet) with a resolution of  $2 \text{ cm}^{-1}$ . UV spectra were measured on “Specord M-40” spectrometer. The spectra of solvents were subtracted using a standard OMNIC program. The CD spectra were obtained on spectropolarimeter JASCO, J-600. Chiral GLC analyses<sup>21</sup> of the amino acids were performed on a Chirasil-L-Val type phase, by using *n*-propyl esters of *N*-trifluoroacetyl derivatives of amino acids. All manipulations were performed under dried and deoxygenated argon.  $\text{CHCl}_3$  was distilled from  $\text{CaH}_2$  and kept over molecular sieves. Reactions were carried out in a flame-dried round-bottomed flasks equipped with a magnetic stirring bar and a water-cooled reflux condenser. All the reagents, including 2,2'-dihydroxy-1,1'-binaphthyl (BINOL, **31b**), 2,2'-diamino-1,1'-binaphthyl (**31c**), and solvents were purchased from Aldrich unless indicated otherwise. TADDOL (**30**) and NOBIN and iso-NOBIN derivatives **31a**,<sup>19h</sup> **31d**,<sup>19g</sup> **31e**,<sup>19h</sup> **32a**,<sup>7b</sup> **32b**,<sup>7b</sup> and **32g**<sup>7b</sup> were available from previous work. The crystallographic data for **1** and **3a** are presented in Table 1. Structures were solved by direct method and refined by full-matrix least squares against  $F^2$  in the anisotropic (H-atoms isotropic) approximation using SHELXTL-97 package. The analysis of the Fourier electron density synthesis have revealed that N(1)-C(5) and C(7)-C(12) rings in the ligand in **2** are disordered by two positions, which were included in refinement in anisotropic approximation with equal occupancies. All hydrogen atoms in the ordered part in **1** and **2** were located from the electron density difference synthesis and were included in the refinement in isotropic approximation. The X-ray data for **32b**, **32d**, and **32f** were obtained at 150K using Oxfor Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo  $K_\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ), a graphite monochromator, and the  $\phi$  and  $\omega$  scan mode. The enantiomeric purity of amino acids was determined by chiral GLC analysis on chiral Chirasil-Val columns.

**Investigation of the Interaction of Sodium NOBIN-ate with **1** by NMR.** Four samples were prepared in CD<sub>2</sub>Cl<sub>2</sub> as follows: A: a solution of sodium salt of (*R*)-NOBIN (0.157M), generated from NaH; B: a saturated solution of Ni-PBP-Gly (0.0088M; 0.7 mL); C: solution B (0.7 mL) was mixed with of solution A (0.04 mL) directly in the NMR sample tube immediately before recording; D: solution A (0.08 mL) was added directly to the NMR tube containing solution C immediately before recording.

**Solubility Experiments.** The concentration of the saturated solution of Ni-PBP-Gly, **1**, [ $\lg \epsilon (\lambda_{\text{nm}})$  3.6 (453 nm)] was estimated as 0.00237 M. Four solutions (1 mL each) of (*R*) or *rac*-NOBIN of 0.01M, 0.05M, 0.1M, 0.15M concentration, respectively, in 1,2-dichloroethane were prepared and sodium hydride (100 equiv relative to NOBIN) was added under Ar. After stirring for 5 minutes, solid **1** (0.1 mg, 0.24 mmol) was added to each sample. The sample were vigorously stirred for 1 h and then filtered in order to determine their molar concentration by UV. The dependence of solubility of **1** on the concentration of the sodium salt of NOBIN was found to be a straight line with  $b = 0.391$  and  $S = \pm 0.008$  obtained by the least square method.

**Ni-PBP-Gly (**1**):** was synthesized using a modification of a procedure described previously.<sup>7a</sup> To a stirred solution of **7** (70.0 g, 0.232 mol or an equivalent of its hydrochloride), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (74.2 g, 0.255 mol) and glycine (19.14g, 0.258 mol) in MeOH (400 mL) was added a solution of KOH [71.4 g, 1.28 mol (greater amounts if hydrochloride of **7** was used)] in MeOH (250 mL). The mixture was refluxed for an additional 30 min, cooled to room temperature and AcOH (72 mL) was added. The solution was diluted with water (1 L) and a red-colored precipitate of **1** was filtered off, washed with distilled water (3 × 150 mL) and dried on air, giving **1** (93.6 g, 0.225 mol, 97%). This complex was used, without any purification, in a large-scale alkylation reaction; **1** can be purified by crystallization from CHCl<sub>3</sub> and dried over anhydrous P<sub>2</sub>O<sub>5</sub>: mp >280 °C (decomp.), [an authentic sample<sup>7a</sup> had mp >280 °C (dec.)]. Anal. Calcd for C<sub>21</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>Ni: C, 60.62; H, 3.63; N, 10.10. Found: C, 60.58; H, 3.60; N, 10.05.

**Ni-PBP-(±)-Ala (±)-(**2**)** was synthesized in an analogy with the above procedure from PBP (**7**), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and (±)-alanine in 95% yield: mp >276–278 °C (dec.); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  1.56 (d,  $J = 6.4$  Hz, 3H, CH<sub>3</sub>), 4.02 (q,  $J = 6.4$  Hz, 1H, CH), 6.77–8.94 (m, 13H, Ar); UV (C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>) log $\epsilon$  ( $\lambda_{\text{max}}$ ) 3.62 (453 nm); IR (KBr) 1675 (carboxyl), 1610 (amide II); 1645cm<sup>-1</sup> (amide I) cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub>Ni·0.5H<sub>2</sub>O: C, 60.14; H, 4.10; N, 9.57; Ni, 13.37; Found: C, 60.37; H, 4.17. N, 9.57; Ni, 14.15.

**Ni-PBA-Gly (**3**):** A 4M MeONa solution in MeOH (35 mL, 0.13 mol) was added to a mixture of PBA **11** (3.1 g, 13.7 mmol), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (8.12 g, 28 mmol) and glycine (2.1 g, 28 mmol) in MeOH (50 mL) and the mixture was stirred at 50 °C for 1 h. Aqueous AcOH (8 mL in 200 mL of H<sub>2</sub>O) was added to the resulting red-colored solution and the red-colored precipitate was filtered and washed with water to give **3** (4.30 g, 12.6 mmol, 92%). This wet product was dried first in the air and then in vacuo at 110 °C for 24 h to remove traces of water or alcohol remained, affording pure **3** (4.0 g, 11.8 mmol, 86%): mp 310–312 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.31 (s, 2H, CH<sub>2</sub>), 7.04 (t,  $J = 7.0$  Hz, 1H, Ar), 7.35 (d,  $J = 6.7$  Hz, 1H, Ar), 7.45 (m, 2H, Ar), 7.63 (s, 1H, CH=N), 7.86 (d,  $J = 7.5$  Hz, 1H, Ar), 7.98 (t,  $J = 7.5$  Hz, 1H, Ar), 8.23 (d,  $J = 5.3$  Hz, 1H, Ar), 9.15 (d,  $J = 8.5$  Hz, 1H, Ar); UV (C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>): log $\epsilon$  ( $\lambda_{\text{max}}$ ) 3.56 (451 nm). Anal. Calcd for C<sub>15</sub>H<sub>11</sub>N<sub>3</sub>NiO<sub>3</sub>: C, 52.99; H, 3.264; N, 12.36. Found C, 53.18; H, 3.21; N, 12.19.

**Ni(II) Complex Derived from the Schiff Base of PBA and (±)-2-Aminopropanoic Acid [Ni-PBA-(±)-Ala] (±)-(4):** was prepared by using a previously described procedure:<sup>6b</sup> mp 286 °C (dec.) (lit.<sup>6b</sup> gives mp 286 °C dec.); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.7 (d, *J* = 7.1 Hz, 3H, Me), 4.16 (q, *J* = 7.1 Hz, 1H, CH), 7.04 (m, 1H, Ar), 7.35 (d, *J* = 6.7 Hz, 1H, Ar), 7.45 (m, 2H, Ar), 7.65 (s, 1H, CH=N), 7.86 (d, *J* = 7.5 Hz, 1H, Ar), 7.98 (t, *J* = 7.8 Hz, 1H, Ar), 8.26 (d, *J* = 5.3 Hz, 1H, Ar), 9.15 (d, *J* = 8.5 Hz, 1H, Ar); UV (C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>): log $\epsilon$  ( $\lambda_{\max}$ ) 3.51 (451 nm).

**Pyridine-2-carboxylic Acid(2-benzoyl-phenyl)-amide (7).** Thionyl chloride (56.0 g, 0.50 mol) was added dropwise to a stirred mixture of picolinic acid **5** (61.5 g, 0.50 mol) and Et<sub>3</sub>N (76.0 g, 0.75 mol) in CH<sub>2</sub>Cl<sub>2</sub> (350 mL) at 0 °C. The stirring was continued for 20 min and then a suspension of *o*-aminobenzophenone **6** (97.5 g, 0.50 mol) in CH<sub>2</sub>Cl<sub>2</sub> (200 mL) was added to the reaction mixture at 0 °C. The stirring was continued for another 2 h at room temperature and the reaction mixture was left standing overnight. A saturated aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (200 mL) was then added slowly over a period of 3 h while stirring, and the neutralization was completed *via* adding dry Na<sub>2</sub>CO<sub>3</sub> (50 g) under stirring. The organic layer was separated, washed with water (3 × 100 mL) and evaporated under reduced pressure. The solid residue was dissolved in acetone and the solution was filtered and evaporated. The crude product thus obtained was crystallized from an acetone-benzene mixture to afford PBP **7** (128.2 g 85%): mp 158–159 °C (an authentic sample<sup>20</sup> had mp 154–156 °C); IR (KBr): 1690 (C=O), 1590 cm<sup>-1</sup> (amide). Anal. Calcd for C<sub>19</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: C, 75.48; H, 4.67; N, 9.27. Found: C, 75.59; H, 4.68; N, 9.23.

**Methyl 2-[(Pyridinecarbonyl)-amino]-benzoate (9).** Thionyl chloride (29.0 mL, 44.8 g, 0.40 mol) was added dropwise to a stirred solution of picolinic acid **5** (49.6 g, 0.40 mol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) at 0 °C during 20 min. The stirring was continued for 45 min at room temperature and then a solution of methyl *o*-anthranilate **8** (39 mL, 45.6 g, 0.30 mol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was added to the reaction mixture over a period of 1 h at 0 °C. The stirring was continued for another 1.5 h at 20 °C and the mixture was then slowly poured into a saturated aqueous solution of Na<sub>2</sub>CO<sub>3</sub>. The organic layer was separated, the aqueous layer was extracted with CHCl<sub>3</sub> (2 × 50 mL), and the organic layers were combined, washed with water, dried (MgSO<sub>4</sub>), and evaporated under reduced pressure. The bright-brown residue was crystallized from EtOH (40 mL) and dried over P<sub>2</sub>O<sub>5</sub> to furnish **9** (44.3 g, 0.17 mol, 58%): mp 84–86 °C (an authentic sample<sup>6b</sup> had mp 86 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200MHz) δ 3.96 (s, 3H), 7.10–8.97 (m, 8H), 13.15 (s, 1H).

**Pyridine-2-carboxylic Acid(2-hydroxymethyl-phenyl)amide (10).** LiBH<sub>4</sub> (8.56 g, 0.388 mol) was added to a stirred solution of methyl 2-[(pyridinecarbonyl)-amino]benzoate **9** (25.1 g, 0.098 mol) in THF (250 mL) at 20 °C, the mixture was stirred for 4 days and then poured into an 8% aqueous KOH (100 mL). The resulting mixture was extracted with CHCl<sub>3</sub> (4 × 30 mL), the chloroform extracts were combined and evaporated. The bright yellow residue was crystallized from EtOH (20 mL), and the mother liquor was additionally purified by column chromatography, using hexane-ethyl acetate (1:1) as eluent to give **10** (4.4 g (0.019 mol, 19%): mp 139–141 °C (an authentic sample<sup>6b</sup> had mp 141 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200MHz) δ 1.22 (s, 1H), 4.76 (s, 2H), 7.11–8.63 (m, 8H), 10.97 (s, 1H).

**Pyridine-2-carboxylic Acid(2-formyl-phenyl)-amide (11).** A solution of DMSO (5.38 mL, 0.076 mol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was slowly added to a stirred solution of oxalyl chloride (3.32 mL, 0.038 mol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) at –60 °C and the stirring continued for 20

min at that temperature. Pyridine-2-carboxylic acid(2-hydroxymethyl-phenyl)-amide **10** (4.4 g, 0.019 mol) was added and the mixture was stirred for 1 h at  $-40\text{ }^{\circ}\text{C}$ .  $\text{Et}_3\text{N}$  (13.22 mL, 0.095 mol) was then added at  $-60\text{ }^{\circ}\text{C}$ , the reaction mixture was allowed to warm to a room temperature and left overnight.  $\text{CHCl}_3$  (20 mL) was added and the mixture was poured into a saturated aqueous solution of  $\text{Na}_2\text{CO}_3$  and the product was extracted with  $\text{CHCl}_3$  ( $4 \times 50\text{ mL}$ ). The organic layers were combined, washed with water, dried ( $\text{MgSO}_4$ ), and evaporated under reduced pressure. The orange-colored residue was crystallized from EtOH (20 mL) to furnish PBA **11** (3.1 g, 72%): mp  $123\text{--}124\text{ }^{\circ}\text{C}$  (an authentic sample<sup>6b</sup> had mp  $124\text{ }^{\circ}\text{C}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200MHz)  $\delta$  7.11–9.63 (m, 8H, Ar), 10.10 (s, 1H, CHO), 13.08 (s, 1H, NH). Anal. Calcd for  $\text{C}_{13}\text{H}_{10}\text{O}_2\text{N}_2$ : C, 69.02; H, 4.46; N, 12.38. Found C, 68.89; H, 4.46; N, 12.38.

**Ni-PBP-Phe (12a).** Benzyltriethylammonium bromide (0.130 g, 0.48 mmol), NaOH (0.96 g, 24 mmol) and benzyl bromide (0.86 g, 5.0 mmol) were added to a suspension of **1** (2.0 g, 4.8 mmol) in  $\text{CH}_2\text{Cl}_2$  (3 mL) under nitrogen and the mixture was stirred at room temperature for 4 h. AcOH (3 mL) was then added, the solvent was evaporated, and the residue was treated with water to form crystalline material that was isolated by filtration. The crude product (**12a**) was crystallized from a mixture of acetone and benzene to afford pure ( $\pm$ )-**12a** (2.30 g, 4.54 mmol, 95%): mp  $276\text{--}277\text{ }^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.86 and 3.13 (ABX system, 2H,  $\text{CH}_2$ ,  $J_{\text{AB}} = 13.7\text{ Hz}$ ,  $J_{\text{AX}} = 2.9$ ,  $J_{\text{BX}} = 5.7\text{ Hz}$ ), 4.36 (ABX system,  $J_{\text{AX}} = 2.9$ ,  $J_{\text{BX}} = 5.7\text{ Hz}$  1H), 6.78–6.83 (m, 2H, Ar), 6.86 (t,  $J = 7.2\text{ Hz}$ , 1H, Ar), 7.17 (m, 3H, Ar), 7.29–7.37 (m, 3H, Ar), 7.42 (d,  $J = 7.2\text{ Hz}$ , 2H, Ar), 7.58 (m, 3H, Ar), 7.7 (d,  $J = 5.0\text{ Hz}$ , 1H, Ar), 7.78 (d,  $J = 7.2\text{ Hz}$ , 1H, Ar); 7.9 (t,  $J = 8.1\text{ Hz}$ , 1H, Ar); 8.73 (d, 1H, Ar.); IR  $\nu$  1665 (COO) 1644 (amide), 1608 (C=N); 1592 (amide), 1549 (Ar)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{28}\text{H}_{21}\text{N}_3\text{O}_3\text{Ni}$ : C, 66.40; H, 4.15; N, 8.30. Found: C, 66.46; H, 4.10; N, 8.22.

**Ni(II) complex Derived from Schiff Base of PBP and Allylglycine ( $\pm$ )-(**12b**). A Large Scale Experiment.** Allyl bromide (16.1g, 11.5 mL, 0.133 mol) was added dropwise to a stirred suspension of **1** (50 g, 0.12 mol), NaOH (24 g, 0.60 mol), and  $\text{Bu}_4\text{NBr}$  (3.2 g, 10 mmol) in  $\text{CH}_2\text{Cl}_2$  (270 mL) under  $\text{N}_2$  and at  $0\text{ }^{\circ}\text{C}$ . The temperature of the mixture was immediately raised to  $30\text{ }^{\circ}\text{C}$  and after 5 min of stirring at that temperature the mixture was cooled and stirred for an additional 1 h at ambient temperature. The reaction was quenched by AcOH (40 mL, 0.60 mol) at  $0\text{ }^{\circ}\text{C}$ , the solvent was evaporated, water was added to the residue and the crystals were collected and washed with hexane (50 mL) and dried in the to furnish ( $\pm$ )-**12b** (54.0g, 0.118 mol, 98%) of sufficient purity. The amino acid obtained by decomposition of the complex was of high purity so that purification of the latter complex was unnecessary. However, crystallization from a benzene-methanol mixture, mp  $232\text{--}235\text{ }^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.52 (m, 2H,  $\text{CH}_2$ ), 4.11 (m, 1H, CH), 5.16 (d,  $J = 17.1\text{ Hz}$ , 1H, CHCHH), 5.32 (d,  $J = 10.3\text{ Hz}$ , 1H,  $\text{CH}=\text{CHH}$ ), 6.43 (m, 1H,  $\text{CH}=\text{CH}_2$ ), 6.78–6.82 (m, 2H, Ar), 7.1 (m, 1H, Ar), 7.3 (m, 1H, Ar), 7.35 (m, 1H, Ar), 7.45 (m, 1H, Ar), 7.54 (m, 3H, Ar), 7.91 (d,  $J = 7.5\text{ Hz}$ , 1H, Ar), 8.0 (m, 1H, Ar), 8.22 (d,  $J = 5.3\text{ Hz}$  1H, Ar), 8.93 (d,  $J = 8.7\text{ Hz}$ , 1H, Ar); IR  $\nu$  1665 (COO), 1644 (amide I), 1608 (C=N), 1592 (amide I), 1549 (Ar)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{19}\text{N}_3\text{O}_3\text{Ni}$ : C, 63.20; H, 4.20; N, 9.21. Found: C, 63.24; H, 4.34; N, 9.16.

**Ni-PBP-( $\pm$ )-Aba ( $\pm$ )-(**12c**).** The reaction was conducted as described for the synthesis of **12a**, starting from complex **1** (2.0 g, 4.8 mmol) and using EtI as the alkylating agent; the reaction time was 15 h. The product was crystallized from a mixture of acetone and  $\text{CHCl}_3$  to afford **12c** (2.05 g, 4.6mmol, 96%): mp  $274\text{--}276\text{ }^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ )  $\delta$  1.39 (t,  $J = 7.5\text{ Hz}$ , 3H), 1.74 (m, 1H,  $\text{CH}_2$ ), 1.97 (m, 1H,  $\text{CH}_2$ ), 4.00 (m, 1H; CH), 6.76–6.81 (m, 2H, Ar), 7.07 (d,  $J = 6.9\text{ Hz}$ , 1H, Ar), 7.33–7.38 (m, 2H, Ar), 7.45 (t,  $J = 6.9\text{ Hz}$ , 1H, Ar), 7.49–7.55 (m,

3H, Ar), 7.9 (d,  $J = 7.8$  Hz, 1H, Ar), 8.01 (t,  $J = 7.8$  Hz, 1H, Ar), 8.24 (d,  $J = 5.3$  Hz, 1H, Ar), 8.94 (d,  $J = 8.7$  Hz, 1H, Ar). Anal. Calcd for  $C_{23}H_{19}N_3O_3Ni$ : C, 62.20; H, 4.31; N, 9.46. Found C, 62.61; H, 4.76; N, 9.26.

**Ni-PBP-(±)-Dip (±)-(12d).** The reaction was conducted in DMF with NaOH as a base. The ratios of the reagents were the same as those shown for the synthesis of **12b** (large-scale experiment), using diphenylmethyl chloride as the alkylating agent. The alkylation was complete within 30 min to afford (±)-**12d** (1.747 g, 3 mmol, 95%): mp 320 °C (dec.);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  4.36 (d,  $J = 2.8$  Hz, 1H, CH), 4.86 (d,  $J = 2.8$  Hz, 1H, CH), 6.8-6.9 (m, 3H, Ar), 7.08-7.02 (m, 8H, Ar), 7.28 (m, 1H, Ar), 7.37 (m, 2H, Ar), 7.43-7.58 (m, 3H, Ar), 7.62 (d,  $J = 5.3$  Hz, 1H, Ar), 7.69 (d,  $J = 7.5$  Hz, 2H, Ar), 7.81 (d,  $J = 7.9$  Hz, 1H, Ar), 7.93 (t,  $J = 7.5$  Hz, 1H, Ar); 8.41 (d,  $J = 8.8$  Hz, 1H, Ar). Anal. Calcd for hydrate  $C_{34}H_{25}N_3O_3Ni \cdot H_2O$ : C 68.03; H 4.54; N 7.00. Found: C, 68.05; H, 4.22; N, 6.92.

**Ni(II) Complex Derived from the Schiff Base of PBP and (±)-2-Amino-3-methylbutanoic acid (±)-(12e):** *iso*-Propyl iodide (2.50 g, 14.4 mmol) was added dropwise to a stirred mixture of **1** (2.0 g, 4.8 mmol) and NaH (0.60 g, 15 mmol) in DMF (7 mL) at the ambient temperature under Ar or  $N_2$  and the mixture was stirred for 1 h. The reaction was quenched with aqueous AcOH (100 mL), the red-colored crystals were isolated by filtration and crystallized from a methanol-benzene mixture to afford (±)-**12e** (2.10 g, 4.56 mmol, 95%): mp 264-265 °C;  $^1H$  NMR (400MHz,  $CDCl_3$ )  $\delta$  0.79 (d,  $J = 6.5$  Hz, 3H, Me), 1.97 (d,  $J = 6.5$  Hz, 3H, Me), 1.9 (m, 1H,  $CHMe_2$ ), 3.92 (d,  $J = 2.8$  Hz, 1H, CH), 6.77-6.84 (m, 2H, Ar), 7.07 (d,  $J = 6.5$  Hz, 1H, Ar), 7.29 (m, 1H, Ar), 7.35 (m, 1H, Ar), 7.44 (m, 1H, Ar), 7.48-7.56 (m, 3H, Ar), 7.92 (m, 1H, Ar), 8.00 (t,  $J = 7.8$  Hz, 1H, Ar), 8.00 (d,  $J = 5.8$  Hz, 1H, Ar), 8.72 (d,  $J = 8.7$  Hz, 1H, Ar); IR  $\nu$  1668 (COO), 1644 (amide I), 1608 (C=N); 1590 (amide I), 1549 (Ar)  $cm^{-1}$ . Anal. Calcd for  $C_{24}H_{21}N_3O_3Ni$ : C, 62.84; H, 4.65; N, 9.04. Found: C, 62.88; H, 4.59; N, 9.17.

**Ni(II) Complex Derived from the Schiff Base of PBP and 2-Amino-2-benzyl-3-phenylpropanoic Acid (13).** The experiment was conducted as that described for **12e**, starting from **1** (1.0 g, 2.4 mmol) in DMF (3 mL), using NaOH (0.60 g, 15 mmol) as a base and BnBr (1.44 g, 8.4 mmol) as the alkylating agent. The reaction was over within 1 h and the product was crystallized from MeOH-benzene to give **13** (1.15 g, 1.95 mmol, 81%): mp 320 °C (decomp);  $^1H$  NMR (400MHz,  $CDCl_3$ )  $\delta$  2.79 and 3.38 (d,  $J = 15.6$  Hz, 4H,  $2 \times CH_2$ ), 6.67 (d,  $J = 4.0$  Hz, 2H, Ar), 6.85 (d,  $J = 12.5$  Hz, 2H, Ar), 7.00 (t,  $J = 7.5$  Hz, 2H, Ar), 7.22-7.37 (m, 12H, Ar), 7.51 (m, 1H, Ar), 7.77 (d,  $J = 7.5$  Hz, 1H, Ar), 7.85 (d,  $J = 5.3$  Hz, 1H, Ar), 7.9 (m, 1H, Ar); 8.54 (d,  $J = 8.7$  Hz, 1H, Ar); IR  $\nu$  1666 (COO), 1644 (amide I), 1608 (C=N), 1595 (amide I), 1575, 1559, 1540 (Ar)  $cm^{-1}$ . Anal. Calcd for  $C_{35}H_{27}N_3O_3Ni$ : C, 70.50; H, 4.56; N, 7.05. Found: C, 70.50; H, 4.52; N, 6.91.

**Ni(II) Complex Derived from the Schiff Base of PBP and 2-Allyl-2-amino-pent-4-enoic Acid (14).** The experiment was conducted as that described for **12e**, starting with **1** (2.0 g, 4.8 mmol) and allyl bromide (1.74 g, 14.4 mmol); the reaction was over within 1 h and the product crystallized from MeOH-benzene to yield pure **14** (1.4 g, 2.8 mmol, 59%): mp 263-265 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  2.31 (dd,  $J = 15.4, 6.5$  Hz, 2H,  $CH_2$ ), 2.50 (dd,  $J = 15.4, 6.5$  Hz, 2H,  $CH_2$ ), 5.28 (d,  $J = 17.4$  Hz, 2H,  $CH=CHH$ ); 5.34 (d,  $J = 10.6$  Hz, 2H,  $CH=CHH$ ), 6.26 (m, 2H,  $2 \times CH=CH_2$ ), 6.69-6.72 (m, 2H, Ar), 7.30-7.36 (m, 3H, Ar), 7.43-7.54 (m, 3H, Ar), 7.57 (m, 1H, Ar), 7.9 (d,  $J = 7.8$  Hz, 1H, Ar), 7.99 (m, 1H, Ar), 8.38 (d,  $J = 5.6$  Hz, 1H, Ar), 8.72 (d,  $J = 8.7$  Hz, 1H, Ar); IR  $\nu$  1666 (COO), 1642 (amide I), 1609 (C=N);

1595 (amide I), 1574, 1536 (Ar), 1440, 1345 (C=C)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{27}\text{H}_{23}\text{N}_3\text{O}_3\text{Ni}$ : C, 65.36; H, 4.67; N, 8.47. Found: C, 65.65; H, 4.79; N, 8.28.

**Ni(II) Complex Derived from the Schiff Base of PBP and 2-Amino-indane-2-carboxylic Acid (15).** The experiment was conducted as that described for **12e**, starting from **1** and  $o\text{-C}_6\text{H}_4(\text{CH}_2\text{Br})_2$  (1equiv) as the alkylating agent. The reaction time was 1 h and the product was purified by column chromatography ( $\text{SiO}_2$ ,  $\text{CHCl}_3\text{-Me}_2\text{CO}$ , 3:1) to afford **15** (0.80 g, 1.55 mmol, 32%): mp 322-325  $^\circ\text{C}$  (dec.);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.54, 3.74 (AB,  $J = 17.7$  Hz, 4H,  $2 \times \text{CH}_2$ ), 6.57-6.69 (m, 4H, Ar), 6.89-6.98 (m, 7H, Ar), 7.31 (m, 1H, Ar), 7.47 (m, 1H, Ar), 7.92 (d,  $J = 7.5$  Hz, 1H, Ar), 8.0 (m, 1H, Ar); 8.43 (d,  $J = 5.3$  Hz, 1H, Ar), 8.71 (d,  $J = 8.4$  Hz, 1H, Ar); IR  $\nu$  1666 (COO), 1645 (amide I), 1609 (C=N); 1595 (amide I), 1574, 1537 (Ar)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{29}\text{H}_{21}\text{N}_3\text{O}_3\text{Ni}$ : C, 67.22; H, 4.08; N, 8.11. Found: C, 67.11; H, 3.91; N, 8.11.

**Ni(II) Complex Derived from the Schiff Base of PBP and ( $\pm$ )-2-Amino-2-benzylbutanoic Acid ( $\pm$ )-(16).** The first alkylation of **1** with EtI was conducted as described for the synthesis of **12c** (1.8 g, 4.0 mmol), the second alkylation with BnBr (1.5 eq) as described for the synthesis of **12e**. The reaction was over within 0.5-1 h. The product was purified by column chromatography ( $\text{SiO}_2$ ,  $\text{CHCl}_3\text{-Me}_2\text{CO}$ , 5:1) to furnish ( $\pm$ )-**16** (2.0 g, 3.7 mmol, 94%): mp 372-374  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.93 (t,  $J = 7.2$  Hz, 3H, Me), 1.15 (m, 1H,  $\text{CH}_2$ ), 1.83 (m, 1H,  $\text{CH}_2$ ), 3.05 and 3.20 (AB,  $J = 13.7$  Hz, 2H,  $\text{CH}_2$ ), 6.75 (m, 1H, Ar), 6.85-6.9 (m, 2H, Ar), 7.18 (m, 2H, Ar), 7.28-7.33 (m, 2H, Ar), 7.36 (d,  $J = 8.1$  Hz, 1H, Ar), 7.51-7.59 (m, 6H, Ar), 7.77 (d,  $J = 7.8$  Hz, 1H, Ar), 7.86-7.91 (m, 2H, Ar), 8.54 (d,  $J = 8.7$  Hz, 1H, Ar); IR  $\nu$  1663 (COO), 1644 (amide I), 1609 (C=N); 1595 (amide I), 1576, 1540 (Ar)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{30}\text{H}_{25}\text{N}_3\text{O}_3\text{Ni} \cdot 0.5\text{H}_2\text{O}$ : C, 66.33; H, 4.82; N, 7.74. Found: C, 66.30; H, 4.41; N, 7.62.

**Ni(II) Complex Derived from the Schiff Base of PBA and 2-Amino-2-ethylbutanoic Acid (22).** The reaction was conducted as described for **23**, starting from complex **3** (2.0 g, 5.9 mmol) and EtI (2.5 equiv). The reaction was over within 30 min. Analytically pure **22** was obtained after chromatography of its sample on LH-20 ( $\text{C}_6\text{H}_6$ ,  $\text{C}_2\text{H}_5\text{OH}$ ; 1:1) (2.2 g, 5.5 mmol, 94%): mp 322-323  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.18 (t,  $J = 7.2$  Hz, 6H, 2Me), 1.76 (m, 2H,  $\text{CH}_2$ ), 2.03 (m, 2H,  $\text{CH}_2$ ), 7.06 (t, 1H, Ar); 7.39-7.51 (m, 3H, Ar); 7.58 (s, 1H, CH=N); 7.88 (d, 1H, Ar,  $J = 7.5$  Hz); 7.98 (t,  $J = 7.8$  Hz, 1H, Ar), 8.35 (d,  $J = 5.0$  Hz, 1H, Ar), 9.19 (d,  $J = 8.7$  Hz, 1H, Ar); IR  $\nu$  1669 (COO), 1645 (amide I), 1608 (C=N), 1598 (amide I), 1557 (Ar)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}_3\text{Ni} \cdot 0.5\text{H}_2\text{O}$ : C, 56.34; H, 4.98; N, 10.37. Found: C, 56.54; H, 4.38; N, 10.44.

**Ni(II) Complex Derived from the Schiff Base of PBA and 2-Amino-2-isopropyl-3-methylbutanoic Acid (23).** Isopropyl iodide (1.3 mL, 2.2 g, 13 mmol) was added to a stirred suspension of **3** (1.5 g, 4.4 mmol) and NaOH (0.88 g, 22 mmol) in DMF (10 mL) under Ar or  $\text{N}_2$ . The mixture was stirred at room temperature for 1 h and then a 3% aqueous solution of AcOH (100 mL) was added. The red crystals formed were filtered and recrystallized from a methanol-acetone mixture to produce **23** (1.3 g, 3.1 mmol, 70%): mp 222-223  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.16 (d,  $J = 6.8$  Hz, 6H, Me), 1.31 (d,  $J = 6.8$  Hz, 6H, Me), 2.4 (m, 2H, CH), 7.05 (t,  $J = 7.6$  Hz, 1H, Ar), 7.41-7.5 (m, 2H, Ar), 7.7 (s, 1H, CH=N), 7.87 (d,  $J = 7.5$  Hz, 1H, Ar), 7.96 (m, 1H, Ar), 8.34 (d,  $J = 5.0$  Hz, 1H, Ar), 9.19 (d,  $J = 8.7$  Hz, 1H, Ar). Anal. Calcd for  $\text{C}_{21}\text{H}_{23}\text{N}_3\text{O}_3\text{Ni}$ : C, 59.47; H, 5.47; N, 9.91. Found: C, 59.44; H, 5.58; N, 9.80.

**Ni(II) Complex Derived from the Schiff Base of PBA and 2-Amino-indane-2-carboxylic Acid (24).** The reaction was conducted as described for **23**, starting from complex **3** (1.5 g, 4.4 mmol) and *o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>Br)<sub>2</sub> (1 equiv) and was over within 1h. The product was purified by column chromatography (SiO<sub>2</sub>, CHCl<sub>3</sub>-Me<sub>2</sub>CO, 4:1) to afford **24** additionally purified by chromatography on LH-20 (C<sub>6</sub>H<sub>6</sub>/C<sub>2</sub>H<sub>5</sub>OH; 1:1) (1.18 g, 2.7 mmol, 60%): mp 327-330 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.88 and 3.42 (AB, *J* = 17.1 Hz, 4H, 2CH<sub>2</sub>), 6.88-6.99 (m, 2H, Ar), 7.27 (bs, 4H, Ar), 7.41 (s, 1H, CH=N), 7.39-7.43 (m, 1H, Ar), 7.47 (m, 1H, Ar), 7.89 (d, *J* = 7.5 Hz, 1H, Ar), 7.8 (m, 1H, Ar), 8.35 (d, *J* = 5.3 Hz, 1H, Ar), 9.12 (d, *J* = 8.7 Hz, 1H, Ar); IR ν 1672 (COO), 1645 (amide I), 1608 (C=N); 1598 (amide I), 1556 (Ar) cm<sup>-1</sup>. Anal. Calcd for C<sub>23</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub>Ni: C, 62.49; H, 3.88; N, 9.5. Found: C, 62.15; H, 3.74; N, 9.61.

**Ni(II) Complex Derived from the Schiff Base of PBP and 2-Amino-cyclopent-3-enecarboxylic Acid (27).** A typical catalytic experiment<sup>22</sup> was carried out as follows: a solution of complex **14** (74.4 mg, 0.15 mmol) in CHCl<sub>3</sub> (3 mL) was introduced into a reactor. Grubbs catalyst (Cy<sub>3</sub>P)<sub>2</sub>Cl<sub>2</sub>Ru=CHPh (74 mg, 0.084 mmol) in CHCl<sub>3</sub> (2 mL) was added slowly dropwise while the mixture was kept at 60 °C under vigorous stirring. The progress of metathesis was monitored by TLC (SiO<sub>2</sub>, CHCl<sub>3</sub>-acetone, 5:1). The reaction was carried out till the disappearance of starting material **14** (about 4 h). The mixture was then concentration *in vacuo* and the residue was purified by chromatography on silica gel (CHCl<sub>3</sub>-acetone, 5:1) to give complex **27**. Analytically pure **27** was obtained after chromatography of its sample on LH-20 (C<sub>6</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>5</sub>OH; 1:1) (54 mg, 0.11 mmol, 77%): mp 220-221 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.06 (bs, 4H, CH<sub>2</sub>), 4.90 (s, 2H, C=CH), 6.69-8.68 (m, 13H, Ar); IR ν 1668 (COO), 1645 (amide I), 1610 (C=N); 1595 (amide I), 1574, 1536 (Ar), 1442 (C=C) cm<sup>-1</sup>. Anal. Calcd for C<sub>25</sub>H<sub>19</sub>N<sub>3</sub>O<sub>3</sub>Ni 0.5H<sub>2</sub>O: C, 62.93; H, 4.22; N, 8.81. Found: C, 63.19; H, 3.84; N, 8.71.

**(R)-(+)-N-(2'-Hydroxy-[1,1']binaphtalenyl-2-yl)-formamide (R)-(+)-(31f).** A mixture of (R)-NOBIN (R)-(+)-**31a** (0.285 g, 1.00 mmol, >98% ee) and ammonium formate (0.470 g, 10 mmol) in acetonitrile (40 mL) was refluxed for 24 hours. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (30 g) using a toluene-ethyl acetate mixture (4:1) to give (R)-(+)-**31f** as a colorless solid (0.226 g, 72%): mp 128-131 °C (toluene); [α]<sub>D</sub> +18 (*c* 0.1, THF); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, mixture of *E* and *Z* isomers) δ 5.16 and 5.23 (two bs, 1 H), 6.93-7.01 (m, 1 H), 7.26-7.60 (m, 6 H), 7.87-8.08 (m, 4 H), 8.69 and 8.77 (two d, *J* = 9.0 and 11.4 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 112.09 (s), 112.44 (s), 116.59 (d), 117.42 (s), 117.53 (s), 117.83 (d), 118.01 (d), 120.72 (d), 123.74 (d), 123.99 (d), 124.05 (d), 124.12 (d), 125.21 (d), 125.43 (d), 125.68 (d), 125.77 (d), 127.35 (s), 127.45 (s), 127.47 (d), 127.54 (d), 127.61 (d), 127.99 (d), 128.32 (d), 128.35 (d), 128.42 (d), 128.54 (d), 129.00 (s), 129.35 (s), 130.37 (d), 130.92 (d), 131.32 (d), 131.41 (d), 132.70 (s), 133.01 (s), 134.00 (s), 134.92 (s), 137.89 (s), 138.05 (s), 151.79 (s), 152.02 (s), 159.24 (d), 161.34 (d); IR (CHCl<sub>3</sub>) ν 3536 (OH), 3392 (NH), 1695 (C=O), 1598 and 1621 (C=C arom); MS *m/z* (%) 313 (60; M<sup>+</sup>), 295 (5), 285 (100), 268 (29), 267 (18), 256 (14), 254 (9), 239 (17), 134 (7), 133.5 (9), 132.5 (7), 119.5 (11); HRMS for C<sub>21</sub>H<sub>15</sub>NO<sub>2</sub> calcd 313.1103 found 313.1107. Chromatography on Daicel Chiralcel OJ column using a hexane-2-propanol mixture (4:1) showed >98% ee for this product (*t*<sub>S</sub> = 16.5 min, *t*<sub>R</sub> = 26.5 min).

**(R)-(+)-N-(2'-Hydroxy-[1,1']binaphtalenyl-2-yl)-acetamide (R)-(+)-(31g):** Acetic anhydride (0.4 mL, 4.28 mmol) was added to a stirred solution of (R)-NOBIN (R)-(+)-**31a** (0.25g, 0.88 mmol) in benzene (3 mL) and the stirring was continued for another 10 min at ambient temperature. The progress of the reaction was monitored by TLC (SiO<sub>2</sub>, hexane-



EtOAc, 1:1). The resulting mixture was concentrated in vacuum and the residue was purified by flash-chromatography on silica gel (20 g) with a hexane-EtOAc (2:1) to give **(R)-(+)-31g** as a crystalline white solid (0.26g, 90%): mp 205-206 °C,  $[\alpha]_D^{28} +73.8$  (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 1.78 (s 3H), 5.38 (s 1H, NH), 6.9-7.4 (m 8H, Ar), 7.86-8.01 (m 3H, Ar), 8.46 (m, 1H, Ar). Anal. Calcd for C<sub>22</sub>H<sub>17</sub>NO<sub>2</sub>: C, 80.71; H, 5.23; N, 4.28. Found: C, 80.34; H, 5.44; N, 4.14.

**(R)-(+)-N-2,2,2-Trifluoro-(2'-hydroxy-[1,1']binaphthalenyl-2-yl)-acetamide (R)-(+)-31h**. Trifluoroacetic anhydride (0.4 mL, 4.28 mmol) was added to a stirred solution of **(R)-NOBIN (R)-(+)-31a** (200 mg, 0.7 mmol) in benzene (3 mL) and the stirring was continued for another 2 min at ambient temperature. The progress of the reaction was monitored by TLC (SiO<sub>2</sub>, hexane-EtOAc, 5:1). Then the resulting mixture was concentrated in vacuum and the residue purified by flash-chromatography on silica gel (20 g) with a hexane-EtOAc (5:1) to give **(R)-(+)-31h** as a crystalline white solid (230 mg, 90%): mp 143-144 °C;  $[\alpha]_D^{28} +5.08$  (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 4.96 (s, 1H, NH), 6.96-8.57 (m, 12H). Anal. Calcd. for C<sub>22</sub>H<sub>14</sub>NO<sub>2</sub>F<sub>3</sub>: C, 69.29; H, 3.70. N, 3.70. Found: C, 69.25; H, 3.24; N, 3.71.

**(R)-(+)-tert-Butyl (2'-Hydroxy-[1,1']binaphthalenyl-2-yl)-carbamate (R)-(+)-31i**. (BOC)<sub>2</sub>O (220 mg, 0.94 mmol) was added to a stirred solution of **(R)-NOBIN** (300 mg, 1.052 mmol) in benzene (3 mL) and the stirring was continued for another 10 h at 80 °C. The progress of the reaction was monitored by TLC (SiO<sub>2</sub>, hexane-EtOAc, 3:1). The mixture was concentrated *in vacuo* and the residue was purified by flash-chromatography on silica gel (30 g) with a hexane-EtOAc (3:1) to give **31i** (260 mg, 68%). Crystallization from a mixture of benzene and hexane afforded pure **(R)-(+)-31i** as a crystalline white solid (200 mg, 52%): mp 170-172 °C;  $[\alpha]_D^{28} +68.51$  (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 1.36 (s, 9H), 7.02-8.5 (m, 12H) Anal. Calcd for C<sub>25</sub>H<sub>23</sub>NO<sub>2</sub> • ½ C<sub>6</sub>H<sub>6</sub>: C, 79.2; H, 6.1; N, 3.3. Found: C, 79.59; H, 6.32; N, 3.25.

**General Procedure for the Synthesis of 32c, 32d, and 32f**. Acyl chloride (3 mmol) was added to a solution of *iso*-NOBIN **(S)-(-)-32a** (285 mg, 1.00 mmol, >98% ee) in pyridine (5 mL) and the mixture was stirred at room temperature overnight. The reaction was quenched by adding 5% aqueous HCl (20 mL), the dichloromethane phase was separated, and the water phase was extracted with dichloromethane (2 × 5 mL). The combined organic extracts were dried with MgSO<sub>4</sub> and evaporated in vacuum. The residue was dissolved in dry methanol (20 mL), solid Na (20 mg) was added, and the mixture was stirred at room temperature for 24 h. The reaction was quenched by adding water (20 mL) followed by 5% aqueous HCl (10 mL) and the mixture was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were dried with MgSO<sub>4</sub> and evaporated in vacuum. The residue was chromatographed on silica gel (10 g) using toluene-ethyl acetate mixture (9:1) as eluent to give the following products:

**(S)-(-)-N-(2'-Hydroxy-[1,1']binaphthalenyl-8-yl)-isobutyramide (S)-(-)-32c**: mp 209-212 °C (toluene);  $[\alpha]_D -12.8$  (*c* 0.1, THF); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.38 (d, *J* = 6.8 Hz, 3 H), 0.76 (d, *J* = 6.4 Hz, 3 H), 0.80-0.89 (m, 1 H), 5.11 (bs, 1 H), 7.12 (dd, *J* = 8.6 Hz, 1.2 Hz, 1 H), 7.29-7.40 (m, 3 H), 7.52-7.62 (m, 3 H), 7.79 (dd, *J* = 8.2, 1.3 Hz, 1 H), 7.88 (dd, *J* = 7.0, 1.2 Hz, 1 H), 7.94 (d, *J* = 9.0 Hz, 1 H), 7.99 (dd, *J* = 8.2, 1.5 Hz, 1 H), 8.24 (d, *J* = 7.3 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 18.80 (q), 19.11 (q), 36.47 (d), 117.82 (d), 120.93 (d), 121.22 (s), 124.32 (d), 124.72 (d), 125.68 (d), 125.80 (d), 126.58 (d), 127.32 (s), 127.52 (s), 127.77 (d), 128.14 (d), 128.91 (s), 130.51 (d), 131.02 (d), 131.88 (d), 133.37 (s), 133.80 (s), 135.84 (s), 150.69 (s), 175.06 (s); IR (CHCl<sub>3</sub>) ν 3534 (OH), 3403 (NH), 1685 (C=O),

1620 and 1598 (C=C arom); MS  $m/z$  (%) 355 (47;  $M^+$ ), 285 (44), 268 (47), 267 (100), 266 (11), 254 (7), 239 (5), 43 (24); HRMS for  $C_{24}H_{21}NO_2$  calcd 355.1572 found 355.1575.

**(S)-(-)-N-(2'-Hydroxy-[1,1']binaphthalenyl-8-yl)-2,2-dimethyl-propionamide (S)-(-)-(32d):** mp 204-206 °C (toluene);  $[\alpha]_D$  -83 ( $c$  0.1, THF);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  0.46 (s, 9 H), 5.38 (bs, 1 H), 7.11 (d,  $J$  = 8.4 Hz, 1 H), 7.24-7.28 (m, 1 H), 7.29-7.36 (m, 1 H), 7.32 (d,  $J$  = 8.9 Hz, 1 H), 7.51-7.57 (m, 3 H), 7.79-7.84 (m, 2 H), 7.86 (d,  $J$  = 8.9 Hz, 1 H), 8.00 (dd,  $J$  = 7.2, 1.4 Hz, 1 H), 8.07 (dd,  $J$  = 7.8, 1.4 Hz, 1 H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  26.44 (q), 38.96 (s), 118.37 (d), 121.97 (s), 123.03 (d), 124.03 (d), 124.59 (d), 125.66 (d), 126.23 (d), 126.54 (d), 127.53 (d), 127.89 (s), 128.09 (d), 129.23 (s), 130.25 (d), 130.73 (d), 132.41 (s), 132.43 (d), 133.58 (s), 133.64 (s), 135.79 (s), 150.90 (s), 177.30 (s); IR ( $CHCl_3$ )  $\nu$  3536 (OH), 3425 (NH), 1673 (C=O), 1621 and 1597 (C=C arom); MS  $m/z$  (%) 369 (49;  $M^+$ ), 285 (18), 268 (54), 267 (100), 266 (9), 254 (6), 239 (4), 57 (29), 41 (6), 29 (5); HRMS for  $C_{25}H_{23}NO_2$  calcd 369.1729 found 369.1722.

**Adamantane-1-carboxylic Acid (2'-Hydroxy-[1,1']binaphthalenyl-8-yl)-amide (32f):** mp 223-225 °C (toluene);  $[\alpha]_D$  -78.6 ( $c$  0.1, THF);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  0.90-1.06 (m, 6 H), 1.36-1.56 (m, 6 H), 1.66-1.72 (m, 3 H), 5.38 (bs, 1 H), 7.16 (dm,  $J$  = 8.2 Hz, 1 H), 7.26-7.31 (m, 2 H), 7.32-7.37 (m, 1 H), 7.35 (d,  $J$  = 8.8 Hz, 1 H), 7.52-7.57 (m, 2 H), 7.60 (bs, 1 H), 7.80-7.86 (m, 2 H), 7.88 (d,  $J$  = 8.8 Hz, 1 H), 8.01 (dd,  $J$  = 8.2, 1.4 Hz, 1 H), 8.15 (dd,  $J$  = 7.7, 1.4 Hz, 1 H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  27.82 (d), 36.05 (t), 37.59 (t), 40.86 (s), 118.44 (d), 122.02 (s), 122.89 (d), 124.07 (d), 124.68 (d), 125.65 (d), 126.27 (d), 126.35 (s), 126.40 (d), 127.61 (d), 127.81 (s), 128.07 (d), 129.36 (s), 130.29 (d), 130.81 (d), 132.50 (d), 133.49 (s), 133.75 (s), 135.81 (s), 151.06 (s), 176.77 (s); IR ( $CHCl_3$ )  $\nu$  3537 (OH), 3417 (NH), 1662 (C=O), 1621 and 1597 (C=C arom); MS  $m/z$  (%) 447 (37;  $M^+$ ), 362 (9), 285 (4), 268 (38), 267 (100), 135 (77), 107 (6), 93 (18), 81 (7), 79 (21), 67 (10), 55 (7), 41 (5); HRMS for  $C_{31}H_{29}NO_2$  calcd 447.2198 found 447.2205.

**(S)-(+)-N-(2'-Hydroxy-[1,1']binaphthalenyl-8-yl)-4-methyl-benzenesulfonamide (S)-(+)-(32e):** 4-toluenesulfonyl chloride (190 mg, 1.0 mmol) was added to a solution of *iso*-NOBIN (S)-(-)-(32a) (285 mg, 1.0 mmol, >98% ee) and DMAP (20 mg) in pyridine (5 mL) and the mixture was stirred at room temperature overnight. The reaction was quenched by adding 5% HCl (20 mL), the dichloromethane phase was separated and the water phase was extracted with dichloromethane (2  $\times$  5 mL). The combined organic extracts were dried with  $MgSO_4$  and evaporated in vacuum. The residue was chromatographed on silica gel (10 g) using a toluene-ethyl acetate mixture (9:1) as eluent to give (S)-(+)-32e (347 mg, 79%): mp 214-6 °C (toluene);  $[\alpha]_D$  +105 ( $c$  0.1, THF);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  2.29 (s, 3 H), 6.87 (dm,  $J$  = 8.6 Hz, 1 H), 7.02 (dm,  $J$  = 8.4 Hz, 2 H), 7.11-7.14 (m, 2 H), 7.18 (bs, 1 H), 7.24-7.28 (m, 1 H), 7.35 (dd,  $J$  = 7.0, 1.3 Hz, 1 H), 7.37-7.45 (m, 3 H), 7.53-7.60 (m, 2 H), 7.67 (dd,  $J$  = 8.2, 1.2 Hz, 1 H), 7.93-7.97 (m, 2 H), 8.03 (d,  $J$  = 9.0 Hz, 1 H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  21.45(q), 114.29 (s), 115.90 (d), 118.05 (d), 119.46 (s), 124.03 (s), 124.16 (d), 124.48 (d), 125.30 (d), 126.02 (d), 126.28 (d), 127.52 (d), 127.60 (d), 128.64 (d), 129.05 (s), 129.25 (d), 130.78 (d), 131.58 (d), 132.01 (d), 133.15 (s), 133.66 (s), 135.79 (s), 135.98 (s), 143.48 (s), 150.95 (s); IR ( $CHCl_3$ )  $\nu$  3538 (OH), 3310 (NH), 1621 and 1598 (C=C arom)  $cm^{-1}$ ; MS  $m/z$  (%) 439 (25;  $M^+$ ), 284 (8), 268 (27), 267 (100), 266 (12), 254 (8), 91 (5); HRMS for  $C_{27}H_{21}NO_3S$  calcd 439.1242 found 439.1247.

**Asymmetric Mono-alkylation of Complex 1 under Phase-Transfer Conditions. A Typical Synthetic Procedure, as Illustrated by the Alkylation of Complex 1 with Benzyl Bromide.** A mixture of finely ground NaOH (2.0 g, 50 mmol), complex 1, (2.1 g, 5 mmol), and (*R*)-NOBIN (*R*)-(+)-31a, (144 mg, 0.5 mmol) in anhydrous  $CH_2Cl_2$  (30 mL) was stirred

under Ar for 3 minutes at ambient temperature (15-20 °C). Benzyl bromide (1.0 g, 5.8 mmol) was then added under Ar and the mixture was stirred for an additional 8-10 min. The reaction was quenched by the addition of 10% aqueous AcOH (30 mL) And the mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL). The organic layer was separated and a small part of it was used to determine the ee [97% (*R*)] of crude Phe (Table 3, runs 5, 6). The residue was purified by flash chromatography on silica gel (100 g) to remove unreacted complex **1**, using a CHCl<sub>3</sub>-acetone mixture (5:1) as an eluent to give complex (*R*)-**12a** (2.3 g, 4.5 mmol, 90%) of 97% ee, according to GLC (see above) of the corresponding (*R*)-Phe, released from **12a**. The crude complex was crystallized from a benzene–acetone mixture to give the enantiomerically pure product (*R*)-**12a** (1.9 g, 3.7 mmol, yield 74%): mp 276-277 °C; [ $\alpha$ ]<sub>D</sub><sup>25</sup> –3605 (*c* 1.0, CHCl<sub>3</sub>/MeOH); ee >99.9% (*R*) according to GLC for the amino acid [lit.<sup>7a</sup> gives for **12a** (*R* = Bn) with ee 13% (*S*), [ $\alpha$ ]<sub>D</sub><sup>25</sup> +370 (*c* 1.0, CHCl<sub>3</sub>-MeOH)]; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.86 and 3.13 (ABX system, *J*<sub>AB</sub> = 13.4 Hz, *J*<sub>AX</sub> = 2.9 Hz, *J*<sub>BX</sub> = 5.7 Hz, 2H, CH<sub>2</sub>), 4.36 (ABX system, *J*<sub>AX</sub> = 2.9 Hz, *J*<sub>BX</sub> = 5.7 Hz, 1H), 6.78-6.83 (m, 2H, Ar), 6.86 (m, 1H, Ar), 7.17 (m, 3H, Ar), 7.29-7.37 (m, 3H, Ar), 7.42 (d, *J* = 7.2 Hz, 2H, Ar), 7.58 (m, 3H, Ar), 7.72 (d, *J* = 5.0 Hz, 1H, Ar), 7.78 (d, *J* = 7.2 Hz, 1H, Ar), 7.9 (t, *J* = 7.8 Hz, 1H, Ar), 8.73 (d, *J* = 8.4 Hz, 1H, Ar); UV (CHCl<sub>3</sub>) log $\epsilon$  ( $\lambda_{\max}$ , nm) 2.80(256), 3.79(351), 3.68(455); IR (neat)  $\nu$  685 (COO), 1615 (amide); 1660 (C=N) cm<sup>-1</sup>. Anal. Calcd for C<sub>28</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub>Ni.: C, 66.40; H 4.15; N, 8.30. Found: C, 66.63; H 4.28; N, 8.11.

**Asymmetric Michael Addition of Complex 1 to Acrylates. A Typical Procedure for the Michael Addition as Illustrated by the Synthesis of Ni(II) complex of a Schiff base of PBP and (*S*)-2-Aminopentanedioic Acid 5-Methyl Ester (*S*)-(+)-(**38a**).** A solution of (*R*)-**32b** (118 mg, 0.36 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (35 mL) and the solution was thoroughly purged with Ar, then NaH (96 mg, 2.4 mmol) was added with stirring under Ar at room temperature. After 4 min, the initial complex **1** (1.0 g, 2.4 mmol) was added under Ar with stirring, followed 5 minutes later by an acrylate **37** (13.7 mmol) and the mixture was agitated for an additional 4 min [the progress of the reaction was monitored by TLC (SiO<sub>2</sub>, CHCl<sub>3</sub>-Me<sub>2</sub>CO, 5:1)]. The reaction was quenched with aqueous 10% AcOH (10ml) and CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added to the resulting mixture. The organic layer was separated, washed with water and an aliquote was used to check the ee of the glutamic acid (94%). The remainder of the organic layer was evaporated and the residue was purified by chromatography on a SiO<sub>2</sub> (60 g) column (CHCl<sub>3</sub>-ether-acetone, 3:1:1). The catalyst (*R*)-**32b** was recovered from the first fraction and recrystallized from benzene (60% cy). The main fraction was evaporated giving final Michael adduct (*S*)-(+)-**38a** (960 mg, 80%): Analytically pure sample was obtained after chromatography of its sample on LH-20 (C<sub>6</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>5</sub>OH; 1:1); mp 256-258 °C; [ $\alpha$ ]<sub>D</sub><sup>25</sup> +3200 (*c* 0.02, CHCl<sub>3</sub>, for complex with 94% ee) [lit.<sup>23</sup> gives [ $\alpha$ ]<sub>D</sub><sup>25</sup> +3505 (*c* 0.02, CHCl<sub>3</sub>) for the enantiomerically pure complex]; mp 258-260 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.88 (m, 1H,  $\beta$ -CH<sub>2</sub>), 2.39 (m, 1H,  $\beta$ -CH<sub>2</sub>), 2.55 (m, 1H,  $\gamma$ -CH<sub>2</sub>), 3.20 (m, 1H,  $\gamma$ -CH<sub>2</sub>), 3.56 (s, 3H, OMe), 4.04 (m, 1H,  $\alpha$ -CH), 6.76–8.89 (m, 13H, ArH); UV (CHCl<sub>3</sub>)  $\lambda_{\max}$ /nm (log  $\epsilon$ ) = 306 (3.99), 459 (3.65). Anal. Calcd. for C<sub>25</sub>H<sub>21</sub>N<sub>3</sub>NiO<sub>5</sub>: C 59.80, H 4.22, N 8.37. Found (after recrystallization): C 59.81, H 4.18, N 8.50.

**Ni(II) Complex of a Schiff Base of PBP and (2*S*,4*R*)-2-Amino-4-methylpentanedioic Acid 5-Methyl Ester (2*S*,4*R*)-(+)-(**38b**).** The synthesis was carried out as described for **38a** (see above) starting from complex **1** (0.2 g) and using methyl methacrylate (**37b**) as an alkylating agent and (*S*)-**32b** (15 mol%) as catalyst; the reaction time was 9 min. An aliquot was used to check the ee of 4-Me-Glu (**40b**): (2*S*,4*R*)/(2*S*,4*S*) = 7:1 with 61% and 54% ee, respectively. The latter diastereoisomeric complexes were separated by preparative TLC (SiO<sub>2</sub>, CHCl<sub>3</sub>-Me<sub>2</sub>CO, 6:1). The (2*S*,4*R*)-diastereoisomer (2*S*,4*R*)-(+)-**38b** was obtained

in 60% with 61% ee and  $[\alpha]_D^{25} +1820$  ( $c$  0.02,  $\text{CHCl}_3$ ). Analytically pure **38b** was obtained after chromatography of its sample on LH-20 ( $\text{C}_6\text{H}_6$ ,  $\text{C}_2\text{H}_5\text{OH}$ ; 1:1); mp 274-276 °C [lit.<sup>23</sup> gives mp 278 °C (dec.);  $[\alpha]_D^{25} +3074$  ( $c$  0.02,  $\text{CHCl}_3$ ), for an enantiopure complex].

**Ni(II) Complex of a Schiff Base of PBP and (±)-2-Amino-5-oxo-5-piperidin-1-yl-pentanoic Acid (±)-(38d).** The synthesis was carried out as described for **38a**, starting from complex **1** (2.0 g, 4.8 mmol) and **37d** (1.57 g, 11.3 mmol), using  $\beta$ -naphthol (10 mol%) as catalyst; the reaction was complete in 60 min and afforded (±)-**38d** (2.5 g, 4.5 mmol, 94%): Analytically pure (±)-**38d** was obtained after chromatography of its sample on LH-20 ( $\text{C}_6\text{H}_6$ ,  $\text{C}_2\text{H}_5\text{OH}$ ; 1:1): mp 238-241 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.45 [m, 4H,  $2\text{CH}_2$  (pip)], 1.55 [m, 2H,  $\text{CH}_2$  (pip)], 1.96 (m, 1H,  $\beta$ - $\text{CH}_2$ ), 2.26 (m, 1H,  $\beta$ - $\text{CH}_2$ ), 2.67 (m, 1H,  $\gamma$ - $\text{CH}_2$ ), 3.1 (m, 1H,  $\gamma$ - $\text{CH}_2$ ), 3.2-3.52 [m, 4H,  $2\text{CH}_2$  (pip)], 3.96 (m, 1H,  $\alpha$ -CH), 6.8 (m, 2H, Ar), 7.25 (m, 1H, Ar), 7.32 (m, 2H, Ar), 7.45 (t,  $J$  = 7.5 Hz, 1H, Ar), 7.53 (m, 3H, Ar), 7.93 (d,  $J$  = 7.8 Hz, 1H, Ar), 8.02 (m, 1H, Ar), 8.22 (d,  $J$  = 5.0 Hz, 1H, Ar), 8.95 (d,  $J$  = 8.5 Hz, 1H, Ar). Anal. Calcd. for  $\text{C}_{29}\text{H}_{28}\text{N}_4\text{NiO}_4 \cdot 0.5 \text{C}_6\text{H}_6$ : C 64.67; H 5.26; N 9.43. Found: C 64.87; H 5.36; N 9.01.

**Ni(II) Complex of a Schiff Base of PBP and (±)-2-Amino-4-carbamoyl-butyric Acid (±)-(38e).** The synthesis was carried out as described for **38a**, starting from complex **1** (2.0 g, 4.8 mmol) and **37e** (0.68 g, 9.6 mmol), using  $\beta$ -naphthol (10 mol%) as catalyst; the reaction was complete in 60 min and afforded (±)-**38e** (2.25 g, 4.6 mmol, 96%): Analytically pure (±)-**38e** was obtained after chromatography of its sample on LH-20 ( $\text{C}_6\text{H}_6$ ,  $\text{C}_2\text{H}_5\text{OH}$ ; 1:1): mp 293-294 °C (decomp);  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ )  $\delta$  1.95-2.05 (m, 1H,  $\text{CH}_2$ ), 2.3-2.4 (m, 1H,  $\text{CH}_2$ ), 2.59-2.7 (m, 2H,  $\text{CH}_2$ ), 4.0 (m, 1H, CH), 6.81 (m, 2H, Ar) 7.18 (m, 1H, Ar), 7.2 (m, 1H, Ar), 7.37 (m, 1H, Ar), 7.47 (m, 1H, Ar), 7.52-7.62 (m, 3H, Ar), 7.94 (d,  $J$  = 7.4 Hz, 1H, Ar); 8.05 (m, 1H, Ar), 8.21 (d,  $J$  = 5.4 Hz, 1H, Ar), 8.93 (d,  $J$  = 8.9 Hz, 1H, Ar). Anal. Calcd. for  $\text{C}_{24}\text{H}_{20}\text{N}_4\text{NiO}_4 \cdot 0.5\text{H}_2\text{O}$ : C 58.1; H 4.27; N 11.29. Found: C 58.19; H 4.11; N 11.03.

**Releasing Amino Acids from the Alkylated Complexes and Analytical Data for Chiral and Achiral Amino Acids. A Typical Procedure Illustrated by the Example of 2-Amino-2-ethyl-butanoic Acid (25).** The alkylated complex **22** (1.8 g, 4.56 mmol) was decomposed by refluxing its suspension in a mixture of aqueous 6M HCl (5 mL) and MeOH (6 mL) for 5-10 min until the red color of the solution disappeared, as described earlier,<sup>7a</sup> then the solution was evaporated to dryness. Water was added to the residue and the insoluble material was filtered off, washed with water and dried to afford PBA·HCl. The pH of the aqueous layer was adjusted to 8 using aqueous ammonia and the mixture was extracted with  $\text{CHCl}_3$  ( $3 \times 10$  mL) to remove small amounts of the remaining PBA. The amino acid **25** was recovered from the aqueous solution by the ion-exchange technique (DOWEX-50,  $\text{H}^+$  form) by first absorbing the mixture on the resin in  $\text{H}^+$  form and then, after washing the resin with water, eluting the amino acid with 5% aqueous ammonia. Crystallization from EtOH-water afforded the pure amino acid **25** (0.35 g, 2.6 mmol, 59%): mp 270 °C (dec.); (lit.<sup>24a</sup> gives mp 305-306 °C);  $^1\text{H}$  NMR (400MHz,  $\text{D}_2\text{O}$ )  $\delta$  0.63 (t,  $J$  = 7.3 Hz, 6H, 2Me), 1.49 (m, 2H,  $\text{CH}_2$ ), 1.59 (m, 2H,  $\text{CH}_2$ ). Anal. Calcd. for  $\text{C}_6\text{H}_{13}\text{NO}_2$ : C, 54.94; H, 9.99; N, 10.8. Found: C, 55.28; H, 10.08; N, 10.86.

**A Special Procedure to Release Highly Hydrophobic Amino Acids as Illustrated by the Example of 2-Amino-2-benzyl-3-phenyl-propanoic Acid (18).** 6M Hydrochloric acid (8 mL) was slowly added to a stirred solution of **13** (3.70 g, 6.2 mmol) in MeOH (15 mL) at reflux. The solution was refluxed for 5-10 min upon disappearance of the red color of the complex, the mixture was evaporated, the residue was treated with water (50 mL), and the

resulting precipitate was filtered off. Water was added to the precipitate, the pH of the aqueous solution was brought to 9-10 by aqueous ammonia and the ligand was extracted with benzene. The insoluble 2-amino-2-benzyl-3-phenyl-propanoic acid (**18**) was isolated by filtration (0.45 g, 1.8 mmol, 30%): mp 288-290 °C (dec.) (lit<sup>24b</sup> gives mp 307-308 °C); <sup>1</sup>H NMR (200 MHz, D<sub>2</sub>O for hydrochloride) δ 2.88 and 3.23 (AB, *J* = 15.2 Hz, 4H, 2CH<sub>2</sub>), 6.95-7.07 (m, 10H, ArH); Anal. Calcd. for C<sub>16</sub>H<sub>17</sub>NO<sub>2</sub>·0.5 H<sub>2</sub>O: C, 72.73; H, 6.59; N, 5.30. Found: C, 72.92; H, 6.63; N, 5.11.

**(R)-(+)-2-Amino-3-phenyl-propionic Acid (Phenylalanine) (R)-(+)-(17a)** was released from complex (*R*)-**12a** (1.8 g, 3.6 mmol) as described in the typical procedure (see above) to give (*R*)-Phe (*R*)-(+)-**17a** (0.40 g, 2.4 mmol, 68%), which was analysed by chiral GLC (*ee* >99.9%): mp 288-290 °C (dec.); [ $\alpha$ ]<sub>D</sub><sup>25</sup> +33.2 (*c* 2, H<sub>2</sub>O) [lit<sup>24i</sup> gives [ $\alpha$ ]<sub>D</sub><sup>25</sup> -33.4 (*c* 1.3, H<sub>2</sub>O) for (*S*)-Phe]. Anal. Calcd. for C<sub>9</sub>H<sub>11</sub>NO<sub>2</sub>: C, 65.44; H 6.71; N, 8.48. Found: C, 65.36; H 6.78; N, 8.44.

**2-Amino-pent-4-enoic Acid (AllylGly) (±)-(17b)** was released from complex **12d** (54.0 g, 0.12 mol) as described in the typical procedure (see above). The amino acid was desalted as described for **25** by the ion exchange technique and crystallized from EtOH-water to furnish (±)-**17b** (8.75 g, 0.076 mol, 63%): mp 251 °C (lit<sup>24h</sup> gives mp 251-253 °C); <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ 2.26-2.4 (m, 2H, CH<sub>2</sub>), 3.5 (t, *J* = 5.8 Hz, 1H; CH), 4.97 (m, 2H, CH=CH<sub>2</sub>); 5.46 (m, 1H, CH=CH<sub>2</sub>). Anal. Calcd for C<sub>5</sub>H<sub>9</sub>NO<sub>2</sub>: C, 52.16; H, 7.88; N, 12.17. Found: C, 52.14; H, 7.9; N, 12.18.

**A Modified Procedure to Release Hydrophobic Amino Acids Illustrated by the Example of 2-Amino-3,3-diphenyl-propionic Acid (±)-(17d).** The procedure employed sodium salt of EDTA to remove Ni(II) ions from the aqueous slurry (pH 8-10) of the ligand and the Ni(II) amino acid complex formed by the decomposition of the initial complex **12d** with HCl. Adjusting the pH of the solution to 8-9 with aqueous ammonia, as described earlier for the synthesis of enantiomerically pure Dip, (±)-**17d**,<sup>24c</sup> followed by crystallization from 1M HCl afforded (±)-**17d.HCl** (82%): mp 238-240 °C (lit<sup>24c</sup> gives mp 234-240 °C). Anal. Calcd. for C<sub>15</sub>H<sub>16</sub>NO<sub>2</sub>Cl·0.25H<sub>2</sub>O: C, 63.83; H, 5.89; N, 4.96. Found: C, 63.97; H, 6.15; N, 5.56.

**2-Allyl-2-amino-pent-4-enoic Acid (diallylGly) (19)** was released from complex **14** (1.2 g, 2.4 mmol) as described in the typical procedure (see above) and crystallized from EtOH to furnish 186 mg (1.2 mmol, 50%): mp 267-300 °C; <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ 2.16 (dd, *J* = 14.5, 8.5 Hz, 2H, CH<sub>2</sub>), 2.37 (dd, *J* = 14.2, 6.4 Hz, 2H, CH<sub>2</sub>), 4.96 (m, 4H, 2 × CH=CHH); 5.42 (m, 2H, 2 × CH=CH<sub>2</sub>). Anal. Calcd for C<sub>8</sub>H<sub>13</sub>NO<sub>2</sub>·H<sub>2</sub>O: C, 55.49; H, 8.67; N, 8.01. Found: C, 55.95; H, 8.58; N, 7.88.

**2-Amino-2-benzyl-butyric Acid (α-Ethylphenylalanine) (±)-(20)** was released from complex **16** as described in the typical procedure (see above) in 75% yield: mp 261-262 °C (lit<sup>24g</sup> mp 248-249 °C); <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ 0.68 (t, 3H, Me), 1.52 (m, 1H, CH<sub>2</sub>), 1.77 (m, 1H, CH<sub>2</sub>), 2.71 and 3.01 (d, *J* = 14.5 Hz, 2H, CH<sub>2</sub>), 6.90-7.20 (m, 5H, Ph). Anal. Calcd. for C<sub>11</sub>H<sub>15</sub>NO<sub>2</sub>·0.25H<sub>2</sub>O: C, 66.84; H, 7.84; N, 7.08. Found: C, 66.88; H, 7.79; N, 6.84.

**2-Amino-indan-2-carboxylic Acid (21)** was released from complex **15** (1.0 g, 1.9 mmol) as described in the special procedure (see above), and crystallized from 6M HCl to give 0.12 g (0.6 mmol, 30% after crystallization): mp 298-300 °C (lit<sup>24d</sup> gives mp 298 °C); <sup>1</sup>H

NMR (200 MHz, D<sub>2</sub>O, for hydrochloride)  $\delta$  3.17 and 3.58 (AB,  $J$  = 15.6 Hz, 4H, 2  $\times$  CH<sub>2</sub>), 7.16 (bs, 4H, ArH). Anal. Calcd. for C<sub>10</sub>H<sub>11</sub>NO<sub>2</sub>·HCl·0.5 H<sub>2</sub>O: C, 53.94; H, 5.88; N, 6.29. Found: C, 53.80; H, 5.13; N, 6.24.

**2-Amino-2-isopropyl-3-methyl-butanoic Acid ( $\pm$ )-(26)** was released from complex **23** (1.25 g, 2.9 mmol) as described in the typical procedure (see above) and crystallized from EtOH-water to give 0.25g (1.59 mmol, 55%): mp 290-292 °C (decomp.) (lit<sup>24e</sup> gives mp 295 °C); <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O/D<sub>2</sub>SO<sub>4</sub>)  $\delta$  0.87 (d,  $J$  = 7.2 Hz, 6H, 2  $\times$  Me), 0.93 (d,  $J$  = 7.2 Hz, 6H, 2  $\times$  Me), 2.19 (sept,  $J$  = 7.2 Hz, 2H, 2  $\times$  CH). Anal. Calcd for C<sub>8</sub>H<sub>17</sub>NO<sub>2</sub>: C 60.35; H 10.76; N 8.80. Found: C 60.11; H 10.24; N 8.48.

**2-Amino-cyclopent-3-enecarboxylic Acid (28)** was released from complex **27** (50% yield), mp 290-298 °C (H<sub>2</sub>O/EtOH) (lit<sup>24f</sup> mp 295- 300 °C); <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  2.32 and 2.72 (AB,  $J$  = 16.5 Hz, 4H, 2  $\times$  CH<sub>2</sub>), 5.43 (m, 2H, =CH).

**2-Amino-pentanedioic Acid (Glutamic Acid) (40a)** was released, as described in the typical procedure (see above), from **38a** (the Michael adduct of **1** and methyl acrylate **37a**), to obtain glutamic acid (*S*)-**40a** (87%), which was of 94% ee according to chiral GLC (see above). Recrystallization from MeOH-H<sub>2</sub>O gave 99% ee in 52% yield.

**2-Amino-5-oxo-5-piperidin-1-yl-pentanoic Acid ( $\pm$ )-(40d)** was released, as described in the typical procedure (see above), from the corresponding Michael adduct of **1** and **37d** to obtain the amino acid in 84% yield. Recrystallization from EtOH gave ( $\pm$ )-**40d** (52%): mp 172-173 °C; <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  1.2-1.31 [m, 6H, 3  $\times$  CH<sub>2</sub> (pip)], 1.78 (m, 2H,  $\beta$ -CH<sub>2</sub>), 2.26 (m, 2H,  $\gamma$ -CH<sub>2</sub>), 3.15 [m, 4H, CH<sub>2</sub>(pip)], 3.44 (t,  $J$  = 6.0, 1H,  $\alpha$ -CH). Anal. Calcd. for C<sub>10</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O: C 51.71; H 8.68; N 12.06 Found: C, 51.92; H 8.29 N, 12.19.

## References and Notes

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